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Using Microbial Desalination Cell to Treat Iraqi Wastewater

Abstract- A Three-chambers MDC was made using three identical cubical plexi-glass sections. Each chamber has an effective volume of 35 cm³. An anion exchange membrane (AEM) was used to separate the anode from the desalination chambers while a cation exchange membrane (CEM) was used to separate the cathode from the desalination chambers. Two graphite sheets were used as anode and cathode electrodes. Biotic experiments have included air-cathode MDC fed with synthetic municipal wastewater, Bio-cathode MDC in which the cathode chamber was inoculated with microalgae as an oxygen source and air-cathode MDC was fed with floated oil layer in the anode chamber as an organic source. Maximum power density obtained from the MDC was 121 mW/m². The corresponding current density was 410 mA/m². Maximum power density obtained in this study was in consistency with that presented in previous studies. Maximum coulombic efficiency and charge efficiency achieved were 9% and 165% respectively. The results of this study confirmed the validity of using MDC technology to treat municipal wastewater as well as oil, desalinate brackish water and generate electric power simultaneously. Moreover, the results revealed the possibility of using mixed culture algae, available in the Iraqi environment, in the cathode chamber as an oxygen source to develop more energy efficient MDC. Further study deals with different system configurations and different operating conditions are needed.

Keywords- Microbial desalination cell; Anode; Cathode; Wastewater.

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1. Introduction

Increasing water demands and shortage in supply have led to great depletion in the available freshwater resources. Untreated wastewater is one of the main sources for contamination of both ground and surface water bodies. Wastewater treatment plants are unable to meet the growing water sanitation needs due to the fast population growth and also facing many problems. One of these problems is that traditional wastewater treatment technologies (e.g. activated sludge process) are energy intensive [1]. In addition to wastewater treatment problems, there is a growing need for fresh water. Provision of fresh water has become the main issue with increasing population and dwindling water resources in most regions of the world including Iraq. Freshwater production by desalination is also cost and energy intensive and leads to greenhouse gas emissions [2].

Commercially, there are several technologies that have been well established for desalination applications such as reverse osmosis, electrodialysis, and thermal distillation. The main problem of these technologies is the relatively high-energy demand in forms of electricity or heat. Renewable energies such as solar energy and wind power may be a suitable option to reduce the energy consumption of traditional

desalination technologies. The costs of these technologies are still higher than conventional technologies and such costs prevent them from large-scale application in many situations.[3]

Microbial desalination cell (MDC) is a promising technique to generate clean energy from wastewater accompanied by removing salts from saline water in an environmental friendly way.

Unlike electrodialysis in which an external source voltage is applied to move the ions out of the desalination section. MDC desalination attained with bacteria is generating the required current and potential.

Previous MFC and MDC studies have used glucose, oxalate, butyrate and other easily degradable substrates as well as several toxic and complex organics such as p-nitrophenol, quinoline, selenite, veratryl alcohol, sulphide-rich wastewater and hydrocarbon-contaminated sediments.[4]

In MDC, three beneficial processes occur simultaneously namely desalination, wastewater treatment, and energy production. Bacteria break down the organic matter in the wastewater on the anode and release electrons to the anode electrode and protons into the water. Anion exchange membrane (AEM) that separates the anode from the desalination chamber and prevents any positively charged ions including the produced

protons from leaving the anode chamber leading to that the charge is balanced by anions (Cl^-) that are moved from the desalination chamber to the anode chamber. On the other side, cation exchange membrane (CEM) separates the cathode from the desalination chamber with charge balanced by cations (Na^+) passing from the desalination chamber through the CEM into the cathode chamber. As a result of this process, water is desalinated in the middle chamber without any external energy source required. Moreover, electricity is produced and organic matters in wastewater are degraded by the anodic exoelectrogenic bacteria [3,5,6]

However, Kim and Logan (2011) have shown that MDC performance can be improved even with a non-buffered saline catholyte using an electrodialysis unit comprising 5 pairs of desalting and concentrating cells [7].

MDC with air cathode represents a better option with many advantages such as lower cost, higher reduction potential and beneficial in terms of environmental sustainability. However, air cathode MDC has slow reduction-oxidation kinetics in the ambient conditions in comparison to the other catholytes. In order to overcome this point, expensive catalytic materials like platinum are required to decrease the activation overpotential for oxygen reduction. In addition, energy is required to maintain the dissolved oxygen at a certain level.

To account for this issue, a biocathode can be used. A biocathode is an electrode which utilizes the microbial population presented on its surface or in the catholyte to catalyze the reduction reaction happening [3,8].

There are only a few studies concerning MDC in Iraq. In this paper, a lab scale air cathode MDC was used to investigate the applicability of this technology to treat synthetic municipal wastewater as well as oily wastewater and to desalinate brackish water whose salinity as high as 25000 mg/l, which simulates maximum possible Iraqi surface water salinity, especially in the marshland southern Iraq. The performance of MDC with photosynthetic microalgae as a biocatalyst in the biocathode was also investigated.

2. Materials and Methods

I. MDC configuration

A Three-chamber MDC (Figure 1) was made using three identical cubical plexi-glass sections. Each section was with the outer side length of 5 cm and inner cross-section of 3 cm diameter.

Each section was provided with two openings with 1 cm diameter each with plugs as shown in Figure 2. Anion exchange membrane (AMI7001S) and cation exchange membrane (CMI7000S) were purchased from Membranes International Inc. Both membranes were preconditioned for 24 h by immersing in 5% NaCl solution and washed with DI water before using, to allow for hydration and expansion of membrane according to the instruction of the manufacturer. Two graphite sheets were cut in a circular shape with about 3 cm diameter and used as cathode and anode electrodes. Then, the electrodes were immersed in DI water overnight before using to remove any excess deposits. The working volume of each of cathode, desalination, and anode chambers was about 35 cm³. The MDC was operated in three modes. First was air-cathode MDC mode in which a small air pump was used for cathode aeration. The MDC in this mode was fed with synthetic municipal wastewater. The second was photosynthetic biocathode MDC mode in which the cathode chamber was filled with water containing mixed microalgae culture. The third was air-cathode MDC fed with synthetic oily wastewater mode.

II. Inoculation and wastewater characteristics

At the beginning of the startup stage of biotic experiments, the anode chamber was filled with tap water seeded with flocculated activated sludge collected from the aeration tank of membrane bioreactor municipal wastewater treatment unit. The cathode chamber was filled with tap water. No buffer solution was used. The desalination chamber water contained 25000 mg/l of NaCl dissolved in distilled water. The MDC was operated under cyclic base fed-batch mode with municipal wastewater supplemented with 1200 mg/l sodium acetate, 200 mg/l urea and 40 mg/l K_2HPO_4 during the whole experiments period. Anolyte and catholyte solutions were replaced when the voltage begins to decrease from its steady-state value, forming a complete cycle of operation. The dissolved oxygen concentration in the cathode zone during operation with air-cathode mode was about 8 mg/l. MDCs were operated at ambient temperatures (20 – 35 °C). Experiments were continued over a period of two months.

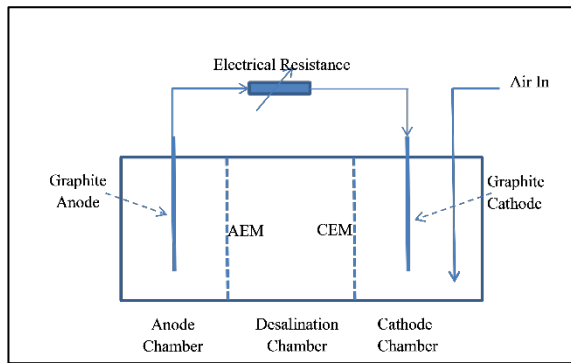


Figure 1: Schematic diagram of the air-cathode MDC

III. Analytical Procedures

The voltage (V) across the external resistance was measured using a digital multimeter. In order to get polarization curves, the external resistance was varied in the range of 10000 - 100 Ω . When the voltage output reached a steady value, current density and power density were calculated according to the projected anodic surface area. All examined variables such as COD concentration; pH, electrical conductivity and dissolved oxygen (DO) were measured using standard methods.

IV. Theory

Coulombic efficiency can be calculated based on the generated charge over all the operation period as follows [9]:

$$CE = \frac{M \cdot \int_0^T I \cdot dt}{F \cdot b \cdot Va \cdot \Delta COD} 100\% \quad (1)$$

where M is oxygen molecular weight (32 g/mole), T is the period of batch mode operation (sec), F is the Faraday's constant (96485 Coulombs/mol electron), b is mole of electrons gained from mole of COD oxidation (4 moles of electrons/mole of COD), Δ COD is the change in COD concentration (g/l) during the period T, Va is the effective volume of the anode chamber.

Charge efficiency is the ratio between the theoretical charge transfers in terms of salt concentrations to the charge harvested and is given as [5]:

$$C_h E = \frac{F \cdot \Delta C \cdot Vd}{\int_0^t I \cdot dt} \cdot 100\% \quad (2)$$

Where Δ C is the change in the molar concentration of the salt solution in the desalination chamber; Vd is effective desalination volume.

Polarization curves were generated to evaluate the relationship between the voltage across the

external resistance and current density during MDC operation. Polarization curves were obtained at different resistance (10000–10 Ω) to visualize the maximum power density and current density can be attained. At the point of maximum power density, the external resistance equals the internal resistance of the MDC. Normally, polarization curves can generally be divided into three zones: (i) starting from the OCV at zero current, there is an initial steep decrease of the voltage: in this zone the activation losses are dominant; (ii) the voltage then falls more slowly and the voltage drop is fairly linear with current: in this zone the ohmic losses are dominant; (iii) there is a rapid fall of the voltage at higher currents: in this zone the concentration losses (mass transport effects) are dominant [9,10].

3. Results and Discussion

I. MDC with air-cathode mode

To conduct the MDC experiments, synthetic wastewater was used to assure constant wastewater characteristics. The COD of the synthetic wastewater was about 1000 mg/l, about four times the COD of normal municipal wastewater. High influent COD wastewater was helped to increase the length of the operation cycle and enhanced MDC operation stability, letting the study to concentrate on desalination and power generation aspects of the MDC. During the first five days, no external electrical resistance was used leaving the anode and cathode electrical terminal at open circuit condition. The previous study regarding MFCs has shown that the biofilm formed on the anode at higher external resistance appeared uniform. Uniform morphology of biofilm facilitates electron generation and transfer [11].

After five days from the beginning of a startup, the electric resistance of 230 ohms was connected between the anode and cathode allowing the electrons to flow from the anode to the cathode. The open circuit voltage (Voc) was recorded when attaining steady state condition in each operating cycle. The development of a steady state during the whole experiment was shown in Figure 2. It was clear that there was a rapid increase in Voc during the first two days of operation and reaching a maximum value of 670 mV after five days. After the addition of the external resistance, the Voc began to decrease reaching a steady value of about 550 mV during the remaining period of the experiment. As it was expected, the pH at the anodes chamber was always higher than 7 while in the cathode chamber was lower than 7. The reduction in Voc

might be attributed to changes happened to the anode biofilm characteristics. The biofilm might represent resistance to substrate diffusion from the bulk solution of the anode chamber to the inner part of the biofilm as well as a resistance to the H^+ ion produced from substrate degradation by microorganisms to diffuse outward from the biofilm to the bulk solution. The value of the V_{oc} across the MDC was in consistency with that presented by other studies [12,13]. The voltage across the external resistance was approximately constant at 60-63 mV (representing a current of about 0.26 mA) during the first 10 days, after that, it was contentiously decreasing to reach about 42 mV (representing 0.18 mA) at the end of the experiment after 32 days from the startup. Voltage reduction was associated with increasingly dark layer on the AEM side-facing anode. This reduction in voltage can be attributed to conductivity reduction in the desalination chamber with time as well as membranes fouling. Figure 3 shows the profile of conductivity of salty water in the desalination chamber with time. About 50% of conductivity reduction was happened during the first nine days of system operation. The rate of conductivity reduction (rate of desalination) was decreasing with time so that the water conductivity in the desalination chamber reached an approximately asymptotic value of about 5 mS/cm after 32 days of system operation. This performance is in consistency with the results presented in other studies [2,14]. It was clear that the MDC system is more suitable to desalinate brackish water with high salt concentration than that with low salt concentration.

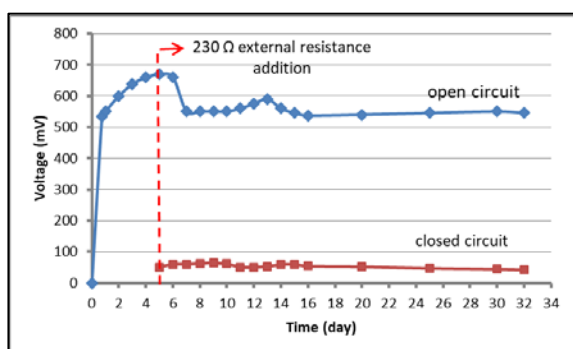


Figure 2: Open and closed circuit voltage of the air-cathode MDC

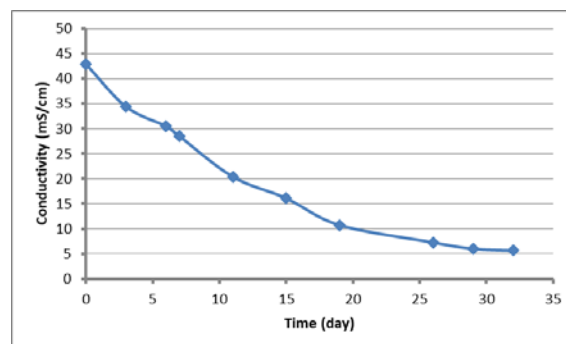


Figure 3: Variation of water conductivity in the desalination chamber with time

The organic matter removal in the anode chamber was monitored in terms of COD removal. On day 11 from the beginning of the experiment, the COD removal during 8 hr. period after feeding with synthetic wastewater was 165 mg/l. At the same duration, the voltage across the external resistance was 51 mV as shown in Figure 2 and the associated change in conductivity in the desalination chamber was 0.33 mS/cm.

The coulombic efficiency is one of the most important indices that were used to describe the MDC performance in terms of power generation. Coulombic efficiency is an index to the quantity of the electrons that were recovered from the substrate in the form of electric current. It was expressed as the ratio of the actual amount of electrons that was gained from the substrate as an electric current flowing in the external circuit to the theoretical amount of electrons which potentially can be delivered by the bacteria based on the COD removal or substrate removal. Coulombic efficiency equals 100% if there is no anaerobic COD removal in the anode chamber by non-electro-active bacteria such as methanogens bacteria.

Using equation 1, the coulombic efficiencies of the air-cathode MDC is about 9%. These values of coulombic efficiency are lower than that presented in other studies [13,15] and might be attributed to the difference in the system dimensions. However, low coulombic efficiency was likely due to the removal of organic matter using oxygen diffusing through the cathode and into the wastewater in the anode chamber, although the use alternate electron acceptors such as sulfate or CO_2 was also possible [16].

Using equation 2 and making use of measured parameters given in the previous section the calculated charge efficiency is 165%. High charge transfer efficiency indicates that in addition to the produced electrical field, salinity gradient across the membranes was another reason for the migration of ions from desalination chamber to the anode and cathode chambers [5].

It was clear from the polarization curves (Figures 4&5) that the maximum power density that can be obtained from MDC was 121 mW/m². The corresponding current densities were 410 mA/m². The maximum power density obtained in this study was in consistency with those presented in other studies [14,15]. The resistances at which the maximum power density attained was about 1000 Ω which should be equal to the internal resistance of the MDC as mentioned above.

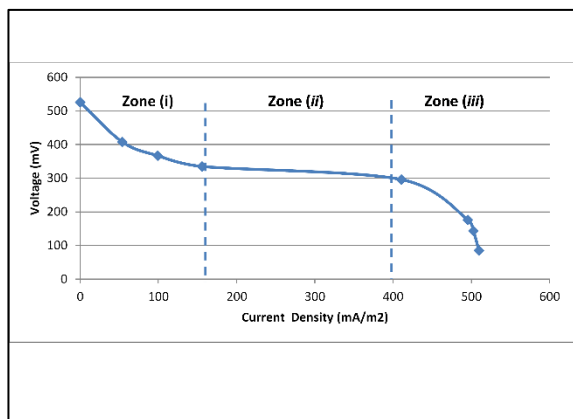


Figure 4: Voltage across external resistance versus current density for air-cathode MDC

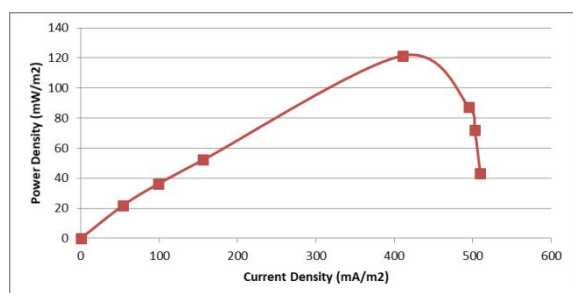


Figure 5: Polarization curve for air-cathode MDC

As mentioned above the voltage across the external resistance had reached maximum value on day 10 from the beginning of the MDC operation. After that, the voltage was contentiously decreasing to reach 42 mV after 32 days from the startup, associated with increasingly dark layer on the AEM side-facing anode. Fouling seems to be the dominant factor causing this voltage reduction. Figure 6 shows photos to the AEM anode side (Figure 6a) covered with a dark brown layer. Ping et al. (2013) and Ebrahimi et al. (2017) showed that such layer is caused mainly by microorganisms (bacteria and fungi) biofilm on the membrane surface [17, 18]. AEM desalination chamber side (Figure 6b) shows a slightly dark brown layer which might be due to microorganism on this side of the AEM membrane occur on diffused nutrient

from the anode chamber to the desalination chamber due to the concentration gradient. A very thin layer of inorganic salt scaling was appeared on the CEM desalination chamber side (Figure 6c) and to a less extent on the CEM side facing cathode (Figure 6d). More investigation is needed to quantify the biofouling and scaling effects on the performance of the MDC.

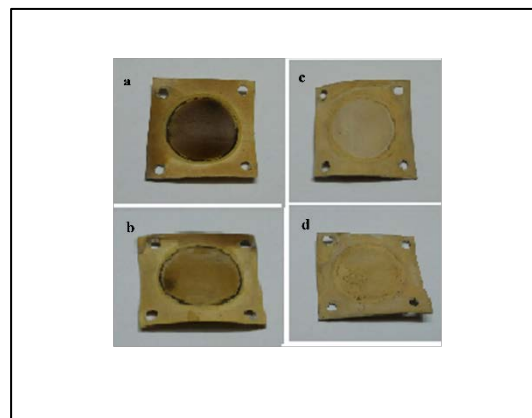


Figure 6: Photographs of fouled ion exchange membranes (after 32 days of operation): (a) AEM facing anode; (b) AEM facing desalination chamber; (c) CEM facing desalination chamber and (d) CEM facing cathode.

II. MDC with photosynthetic microalgae biocathode mode

Preliminary tests to the performance of photosynthetic microbial desalination cells (PMDCs) were done in this work. The MDC was supported by a photosynthetic microorganism, (mixed culture microalgae) as an oxygen source. A mixed culture microalga with MLSS of about 2000 mg/l was added to the cathode chamber after turning off the artificial aeration. Two tests were done with different external electrical resistance which was 230 and 900 Ω , respectively. An electrical 1-watt lamp was used as a light source. The results revealed the efficiency of microalgae to produce oxygen with sufficient amount enough to deplete protons in the cathode chamber when they combine with electrons generated in the anode chamber. Figures 7 and figure 8 show the clear variation of voltage across the external resistance with time under the light on and off conditions. This performance was in consistency with those illustrated by other studies [5, 19, and 20]. Sever CEM was observed at the end of one day of MDC operation with this mode which might be attributed to the tendency of the microalgae to form biofilm on the membrane resulted in membrane blockage and consequently higher membrane internal electrical

resistance and the consequently lower voltage across the external resistance.

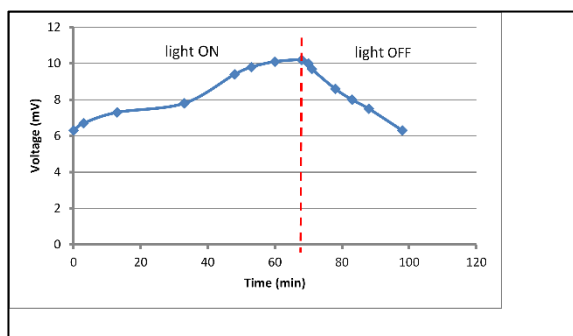


Figure 7: Performance of microalgae biocathode MDC, $R=230 \Omega$.

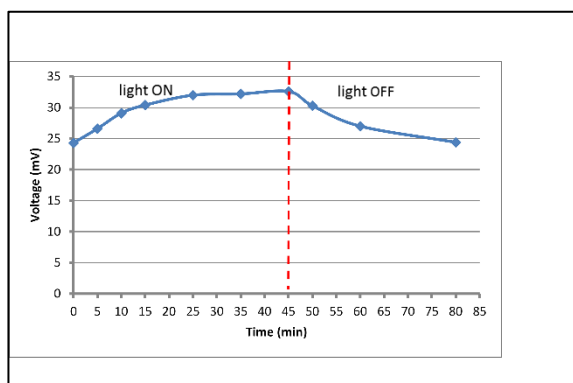


Figure 8: Performance of microalgae biocathode MDC, $R=900 \Omega$.

III. MDC with air cathode mode fed with synthetic oily wastewater

A quantity of crude oil of about 5 ml was poured in the anode chamber forming a floated layer on the anolyte solution that composed initially of distilled water supplemented 1200 mg/l sodium acetate, 200 mg/l urea, and 40 mg/l KH_2PO_4 . The anode chamber was operating as a two-phase partitioning bioreactor in which the petroleum hydrocarbons compounds composed the floated layer was expected to dissolve slowly in the anolyte in such a way sufficient to feed the exoelectrogenic bacteria and keeping their concentrations in the anolyte well below toxicity limits since the MDC was operated normally in this mode of operation. Figure 9 shows the variation of voltage across 330Ω external electrical resistance during 14 days of operation in this mode. The voltage was decreased from 64.9 to 34 mV during the first five days. This period seems to be enough for the microorganism to acclimate to use crude oil as a sole carbon source. After that, there was a rapid increase in voltage across the external electrical resistance reaching about 123 mV after 10 from the beginning of the experiment and remained higher

than 110 mV for the rest period of the experiment.

Figure 10 shows the way in which the voltage across the external resistance varies with current density in comparison with that in the case of air-cathode MDC fed with municipal synthetic wastewater. It was clear that this variation in case of oily floated layer was steeper than that in case of synthetic municipal wastewater. With oily floated layer, no relatively slow varying linear region can be distinguished which implies that the internal ohmic resistance was not dominant in this case. Mass transport and less efficient exoelectrogenic biofilm on the anode might be dominant in the mode of MDC operation. The polarization curve shown in Figure 11 reveals that the maximum power density that can be obtained from MDC in this mode about 64 mW/m^2 . The corresponding current densities were 304 mA/m^2 . Both maximum power density and corresponding current density were less than that of air-cathode MDC fed with municipal wastewater given in section 3.2.1.5 (121 mW/m^2 and 410 mA/m^2 , respectively).

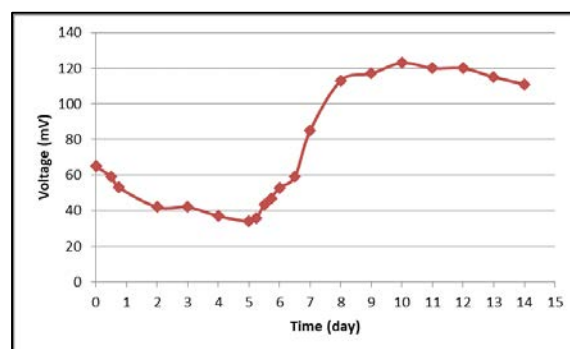


Figure 9: Closed circuit voltage of the air-cathode MDC fed with oily floated layer, $R = 330 \Omega$;

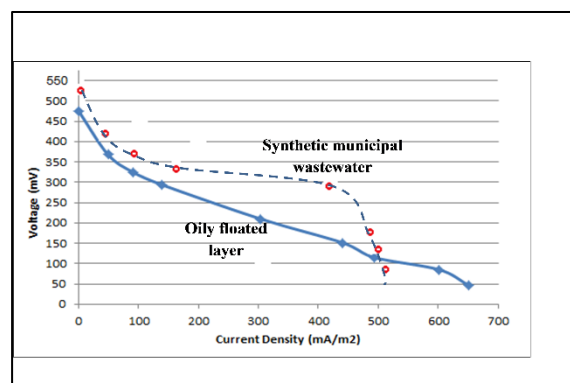


Figure 10: Voltage across external resistance versus current density for air-cathode MDC fed with oily floated layer in comparison with air-cathode MDC fed with synthetic municipal wastewater

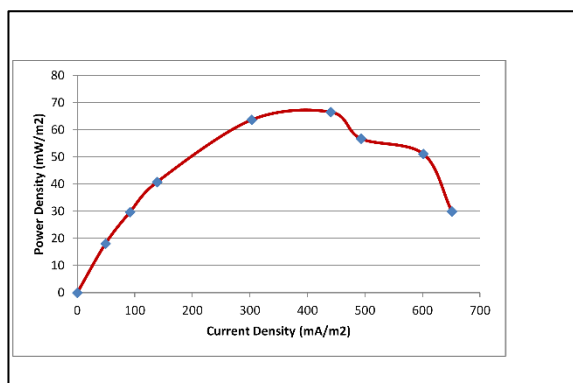


Figure 11: Polarization curve for air-cathode MDC fed with an oily floated layer.

4. Conclusions

The results of this study confirmed the conceptual validity of using MDC to treat municipal wastewater, desalinate brackish water and generate electric power simultaneously under Iraqi conditions. Moreover, the efficiency of using mixed culture algae, available in the Iraqi environment, in the cathode chamber as an oxygen source was proven to be possible to develop more energy efficient MDC despite CEM fouling. A preliminary experiment was done to assess the performance of the air-cathode MDC when using crude oil as a sole organic substrate in the air-cathode MDC. The crude oil was forming a floated layer on the anolyte solution and the anode was operating as a two-phase partitioning bioreactor in which the petroleum hydrocarbons compounds composed where the floated layer was dissolving slowly in the anolyte in such a way sufficient to feed the exoelectrogenic bacteria and keeping their concentrations in the anolyte well below toxicity limits. The power and current density of the MDC were in consistency with that presented in previous studies. However, MDC configuration needs to be optimized.

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